Nucleation and growth of YBaCuO on $SrTiO_3$

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We have studied transmission electron microscopy (TEM) cross sections and plan views of YBaCuO films on $SrTiO_3$ single-crystal substrates at various stages of post-deposition anneal. These TEM studies reveal in extraordinary detail the process of nucleation of epitaxial crystal structure characteristic of the films. In partially annealed samples sputtered from separate Cu, Y, and BaF_2 sources, we see the 2-4-8 phase nucleates at the substrate interface, with the *c* axis parallel to the [001] substrate direction (surface normal). Upon further annealing, the 1-2-3 phase nucleates on this layer with the *c* axis parallel to each of the [100], [010], and [001] substrate directions. Rapid growth in the *a*- and *b*-axis directions results in an uneven "basket weave" surface texture. This information is crucial to the successful control and optimization of crystal orientation and surface morphology of superconducting thin films necessary for the application of this material to multilayer structures for electronic devices.

Recently there has been considerable activity focused on $Y_1Ba_2Cu_3O_{7-\delta}$ superconducting films formed by deposition from fluorine-containing sources.[1-4] These films appear to have greater stability against environmental degradation, particularly in the unannealed state, compared with those from nonfluorine-containing sources. The superconducting phase is formed by annealing at high temperatures (800–900 °C) in the presence of wet oxygen, where the water aids in converting BaF_2 to the oxide phase. A second phase, with metal ratios of 2-4-8, has been observed to form in Cu-rich halogen-containing films.[3,5] This phase, which appears to be an ordered defect structure of the 1-2-3 phase with a *c*-axis length of 27.2 Å, is superconducting with a T_c about 10 K lower than the 1-2-3 phase.

We have successfully grown highly oriented $Y_1Ba_2Cu_3O_{7-\delta}$ on $SrTiO_3$ single-crystal substrates recently.[6] These films are sputter deposited as an amorphous alloy from three separate targets Y, Cu, and BaF_2 and when annealed at 850 °C for 1/2 h in wet oxygen, show sharp ($\Delta T \simeq 1$ K) resistive transitions with zero resistance above 90 K. Further details of the preparation and transport characterization of these films were presented in our original publication.

Successful control of orientation, surface morphology, and crystal quality requires a detailed understanding of the issues of epitaxy, nucleation, and growth of the different phases and orientations in these films. Our present study focuses on the sequence and character of nucleation and growth during the solid-state transformation from the as-deposited amorphous to the crystalline phase. We have performed high-resolution cross section and plan-view transmission electron microscopy (TEM) on samples at several stages of transformation from the amorphous to crystalline state. We see that the first stages of annealing result in large, epitaxial, plate-like crystals of the 2-4-8 phase with the *c*-axis parallel to the [001] surface normal of the substrate, and randomly oriented 1-2-3 phase homogeneously nucleated in the bulk of the film. Further annealing results in 1-2-3 phase epitaxial crystals with the *c*-axis parallel to each of the [100], [010], and [001] substrate directions.

For TEM investigations, the samples were lapped to a thickness of 100 μm and then dimpled to a thickness of 10–30 μm. An argon ion mill was then used to thin the samples to electron transparency. The last 1 h of ion milling was performed at liquid-nitrogen temperatures to attempt to minimize ion damage. The cross-section samples were cemented face to face prior to lapping, dimpling, and ion milling. The microscopy was performed on a Phillips 430 operating at 200 kV. All annealing was performed in flowing wet oxygen.

Figure 1 shows the x-ray diffraction in standard $\Theta - 2\Theta$ geometry for a sample heated at 850 °C for 1 h. In the 850 °C/1 h sample the (00*l*) 1-2-3 phase peaks are observed, as well as (*h* 00) 1-2-3 phase peaks [note that the near coincidence of the 1-2-3 phase (0*k* 0) peaks with the substrate

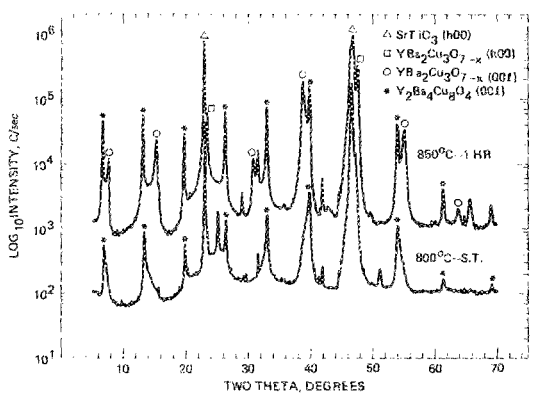

FIG. 1. X-ray diffraction in standard $\Theta - 2\Theta$ geometry for a sample heated at 850 °C for 1 h, and a sample heated to 800 °C and then furnace cooled.

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(00l) peaks masks their presence]. This indicates that the c axis of the 1-2-3 phase occurs with both parallel and perpendicular orientations with respect to the surface normal. We also see the (00l) peaks from the 2-4-8 phase with a c-axis length of 13.6 Å, indicating that this phase is oriented with the c axis parallel to the surface normal. Scanning electron micrographs (SEM) show a rough surface with large rectangular crystals about 1 μm by 10 μm oriented at 90° relative to each other in the plane of the sample. This "basket weave" pattern obviously results from epitaxy from the underlying substrate; however, x-ray diffraction alone is unable to distinguish which of the orientations of phases is responsible.

Also shown in Fig. 1 are the diffraction results for a sample heated to 800 °C and then furnace cooled. The most prominent features are the (00l) peaks from the 2-4-8 phase oriented with the c axis parallel to the surface normal. The 1-2-3 phase peaks are only present as weak shoulders on the 2-4-8 and substrate peaks. This indicates that the 2-4-8 phase grows first during the crystallization process.

In order to further investigate the nucleation and growth in the initial stages of crystallization a sample was annealed to 750 °C and prepared for cross-section and plan-view TEM investigations. Figure 2 shows the cross-section view of this sample. The arrow points to the large flat crystals which have nucleated and grown at the substrate interface. The lattice fringes apparent in these crystals are the c-axis planes of the 2-4-8 phase. These crystals have a heteroepitaxial orientation with their c axis aligned along the [00l] direction of the strontium titanate substrate. The plan-view analysis of this sample showed moiré fringes from the lattice mismatch of these crystals with the substrate and indicated that these epitaxial c-axis oriented 2-4-8 phase crystals covered about 70–80% of the substrate-film interface.

In addition to this epitaxial, c-axis oriented 2-4-8 phase, we saw in both plan view and cross section some randomly oriented, smaller ($\sim$100 Å) 1-2-3 phase crystals which nucleated in the bulk of the film with random orientation. We also observed in the plan-view sample a very small number of needle-shaped crystals, about 2000–3000 Å long by 500 Å wide. These crystals were oriented with the c axis lying in the plane of the sample directed along either the [100] or [010] substrate directions. Similar but larger ($\sim$1 μm by 1000 Å) crystals were also observed in the plan view of a sample heated to 800 °C.

Figure 3 shows the cross-section view of a sample which was annealed at 850 °C for 1 h. Near the bottom of the film there are large flat crystals of both the 1-2-3 and 2-4-8 phase oriented with the c axis parallel to the surface normal. The needle-like crystals which we observed in the partially annealed samples have become huge plates with their c axis lying in the plane of the sample along either the [100] or [010] substrate directions. This 90° orientation of these protruding crystals makes up the basket weave texture observed in SEM. These plates do not contact the substrate but retain their orientation with respect to the substrate by the heteroepitaxial relationship with the c-axis oriented 2-4-8 phase near the interface.

The inset on this figure shows the diffraction pattern taken from an area which includes the substrate, the c-axis oriented 2-4-8 phase, and the a-axis oriented 1-2-3 phase material. The 1-2-3 phase produces closely spaced spots in horizontal rows, with spacing equal to 1/3 the spacing between the substrate spots. This is indicative of the relationship $a_{SrTiO_3} \simeq 1/3 c_{1\text{-}2\text{-}3}$. The 2-4-8 produces closely spaced spots in vertical columns, with spacing equal to 1/3.5 the spacing between the substrate spots. This spacing is a result of the 15% c-axis expansion in the 2-4-8 phase which is reportedly due to an insertion of an extra CuO plane. This

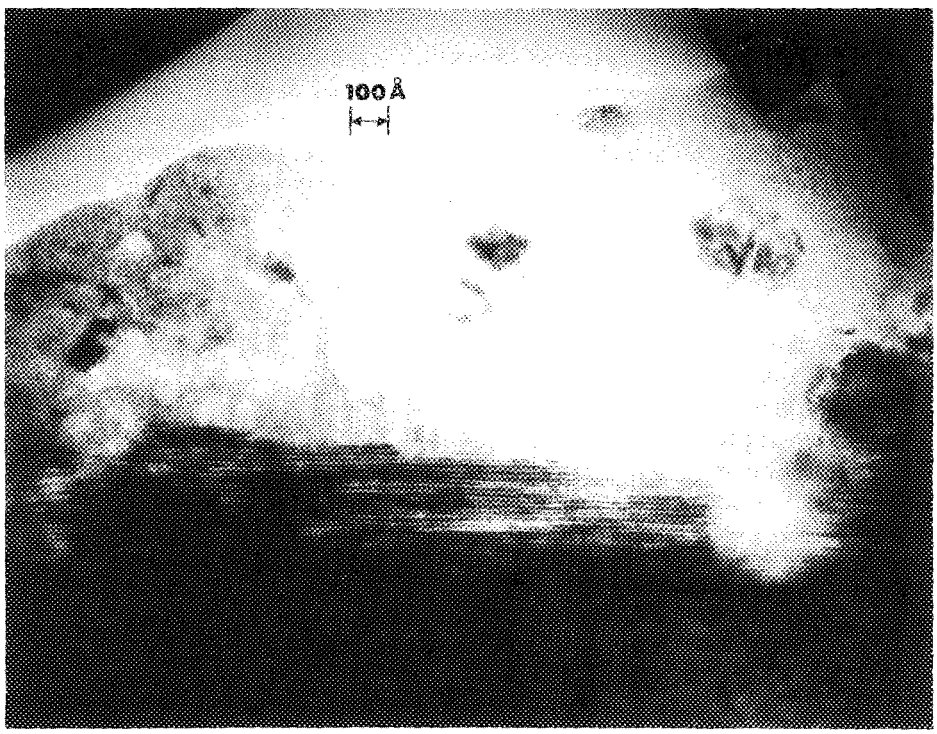

FIG. 2. TEM cross section of a sample heated to 750 °C and then furnace cooled.

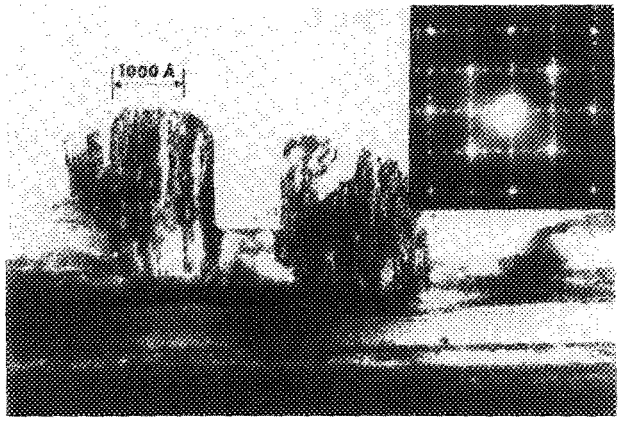

FIG. 3. TEM cross section of a sample heated at 850 °C for 1 h. Inset shows electron diffraction pattern.

diffraction pattern serves as a beautiful demonstration of the orientational relationships between various phases present.

Near the substrate-film interface we see a disordered region. This region was not observed in samples with milder anneals, and thus may be a result of reaction with the substrate.

Our observations of morphology are consistent with crystal growth being slow in the *c*-axis direction relative to the *a*- or *b*-axis directions. Crystals which nucleate at the interface with the *c*-axis normal to the film would then grow rapidly along the interface and nearly cover the interface. The subsequent growth of this epitaxial layer along the *c*-axis direction into the remainder of the film would be slow. Crystals which nucleated with either *a* or *b* axis normal to the substrate could grow much faster resulting in the rectangular crystals which make up the observed basket weave morphology. This hypothesis is further strengthened by the observation of an anisotropy in growth rate during growth of single crystals from the melt.[7]

The observation that the 2-4-8 phase is the first to grow epitaxially in these films may be due to the closer lattice match with the $SrTiO_3$ substrate which has been reported in the literature.[3] We find, from diffraction in the 750 °C sample in plan view that near the substrate there is an epitaxial phase with a lattice constant of 4.3 Å. This differs from reported values of 3.87 Å, and would result in a larger lattice mismatch with the substrate. A second explanation for the first growth of the 2-4-8 phase near the substrate, is that the 2-4-8 phase is stabilized by the presence of fluorine.[5] The fluorine is removed from the film by reaction with the wet oxygen, which must diffuse through the film to reach the interface. This reaction only just begins to occur at 700–800 °C, so fluorine concentrations are likely to be high at the interface during the initial stages of the anneal, resulting in stabilization of the 2-4-8 phase relative to the 1-2-3 phase.

In summary, we have been able to determine that the *c*-axis oriented 2-4-8 phase nucleates and grows rapidly along the substrate interface. Upon further annealing we see *a*-axis oriented 1-2-3 phase material growing heteroepitaxially on this material. The resulting morphology is consistent with growth along the *c* axis being slow relative to that in either the *a*- or *b*-axis directions. The information obtained from these studies should allow us to enhance the growth of a particular orientation of the 1-2-3 phase relative to the other orientations, as well as the less desirable 2-4-8 phase.

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